Electron Paramagnetic Resonance (EPR)

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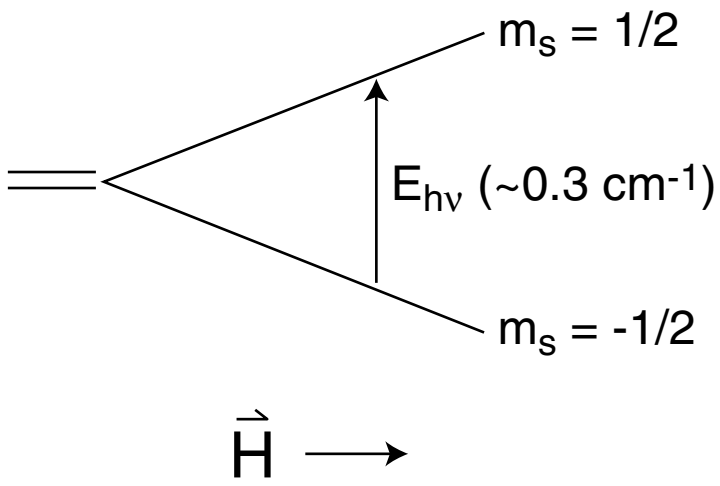
18 April 2001

Electron Paramagnetic Resonance

- unpaired electrons can change their spin state by absorbing microwave energy in the presence of a magnetic field:



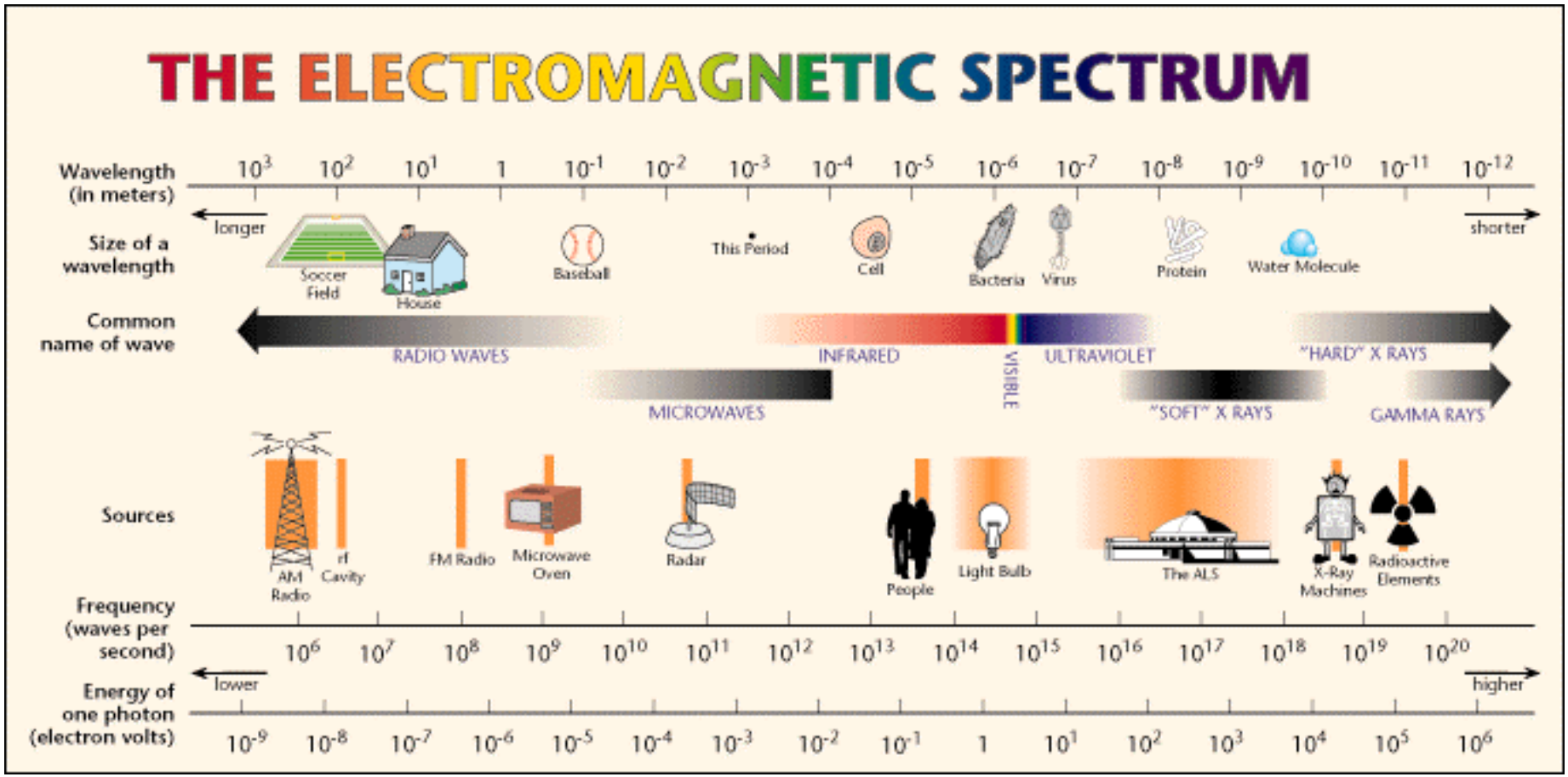
$\Delta m_s = \pm 1$

- Only paramagnetic systems can show EPR signals
  - no interference from diamagnetic background (unlike susceptibility measurements

Common systems:

Certain transition metals (e.g. V, Mn, Fe, Co, Ni, Cu etc.)
Organic radicals (NO•, TEMPO, CH_3• etc.)

Boltzmann distribution dictates initial population differences
-not much at RT with 0.3 cm^{-1} separation



EPR
Resonances
(~0.3 cm^{-1})

History of EPR

1st paper: Zavoisky (J. Phys. USSR, 9, 1945, 221) in Russian

– Wartime technology in microwaves paved the way for peacetime use as a research tool.

Some initial studies on radicals in biological systems:

Commoner et al. (PNAS, 42, 1956, 710-18) saw a light-induced radical signal appear in photosynthetic systems:

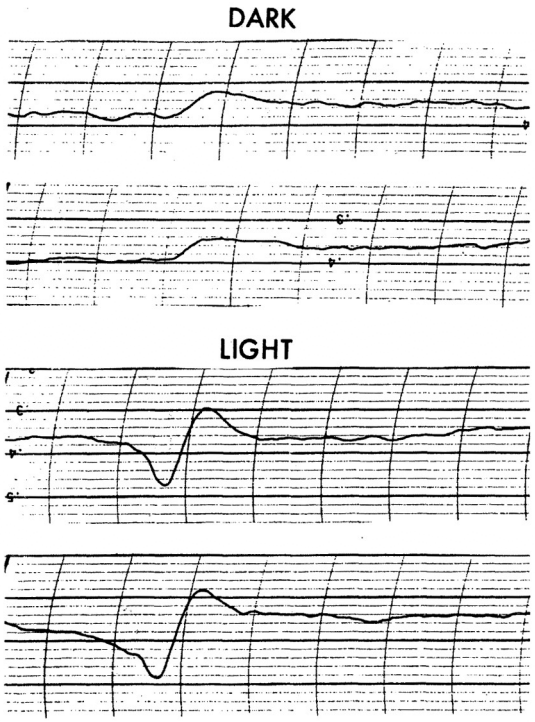


FIG. 1.—Paramagnetic resonance absorption of a chloroplast suspension in the dark (*upper curves*) and in the light (*lower curves*). Magnetic field increases toward the right along the abscissa. The ordinate is the meter deflection, representing the rate of change, with respect to field strength, of the absorption of 9,000-Mc/sec microwave energy by the sample, as the field strength is varied automatically. The curves thus represent derivatives of absorption curves. Each division along the abscissa represents approximately 20 gauss and 30 seconds. The half-width of the resonance is about 10 gauss.

Theoretical Aspects of EPR

$$\text{Hamiltonian} = \underset{\text{A}}{\beta \mathbf{g}\cdot\mathbf{H}\cdot\boldsymbol{S}} - \underset{\text{B}}{\beta_N \mathbf{g}_N\cdot\mathbf{H}\cdot\boldsymbol{I}} + \underset{\text{C}}{\mathbf{A}\cdot\boldsymbol{I}\cdot\boldsymbol{S}}$$

A: Electron Zeeman term

- This is the basic component of an EPR spectrum
  - **g** value is affected by spin-orbit coupling (see below)

B: Nuclear Zeeman term

- Is much weaker than electronic Zeeman term because of the much smaller nuclear magnetic moment (1000x less).

C: Hyperfine interaction

- No magnetic field dependence
- Spin-orbit coupling is a significant contributor to the hyperfine interaction by increasing the 'effective' total electron spin.
  - S.-O. coupling can be quite large for transition metals because of their significant orbital angular momentum.
  - Likewise, it is much smaller for organic radicals.

Hyperfine interaction comes in two parts:

Isotropic (Fermi contact) - overlap of 1s orbital with the nucleus

- valence electrons make their presence known through 'core polarization'

Anisotropic (dipolar) - is important in multi-spin systems and for unpaired electrons in non-symmetric orbitals (p,d).

References:

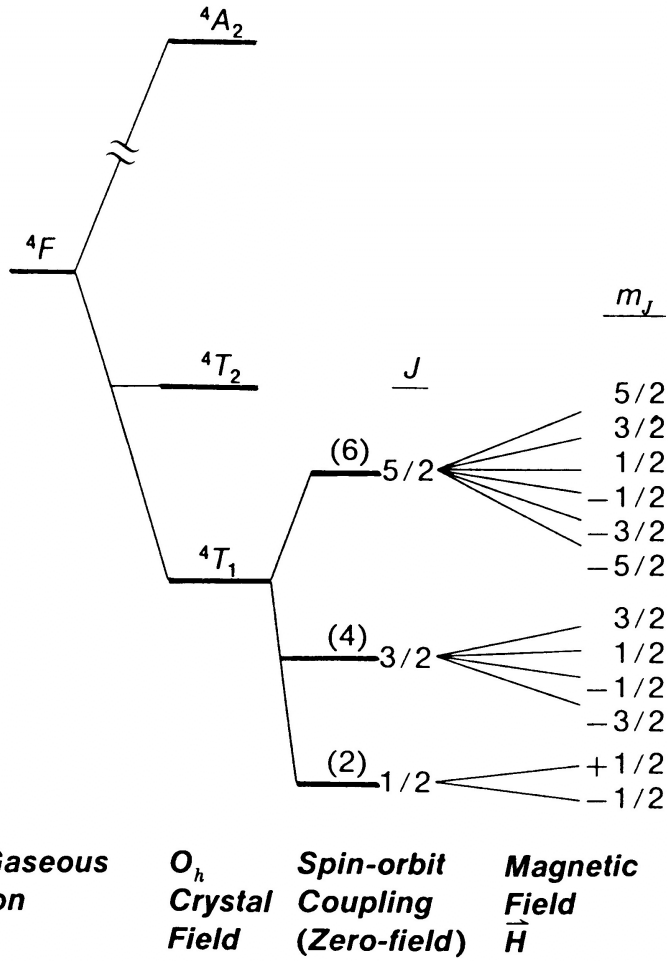
Drago, R.S.; *Physical Methods for Chemists, 2nd edition*, Saunders, 1992, Ch 9 + 13.

Wertz, J.E., Bolton, J.R.; *Electron Spin Resonance: Elementary Theory and Practical Applications*, McGraw Hill, 1972.

Brudvig, G.W.; *Methods. Enzym.*, 246, 536-554.

Feher, G.; *Electron Paramagnetic Resonance with Applications to Selected Problems in Biology*, Gordon & Breach, 1970.

A lot can happen before the magnet is turned on (Zero-field splitting):



$$H = \beta \mathbf{g}\cdot\mathbf{H}\cdot\boldsymbol{S} + D[S_z^2 - ((1/3)S(S+1)] + E/D\,(S_x^2 - S_y^2)$$

D: Axial zero-field splitting term
E: Rhombic zero-field splitting term

Kramer's doublets (±1/2, ±3/2, ±5/2 etc.) exist in non-integer spin systems

Kramer's rule states that Kramer's doublets cannot be separated by zero-field splitting

-Non-integer spin systems quite often show EPR signals

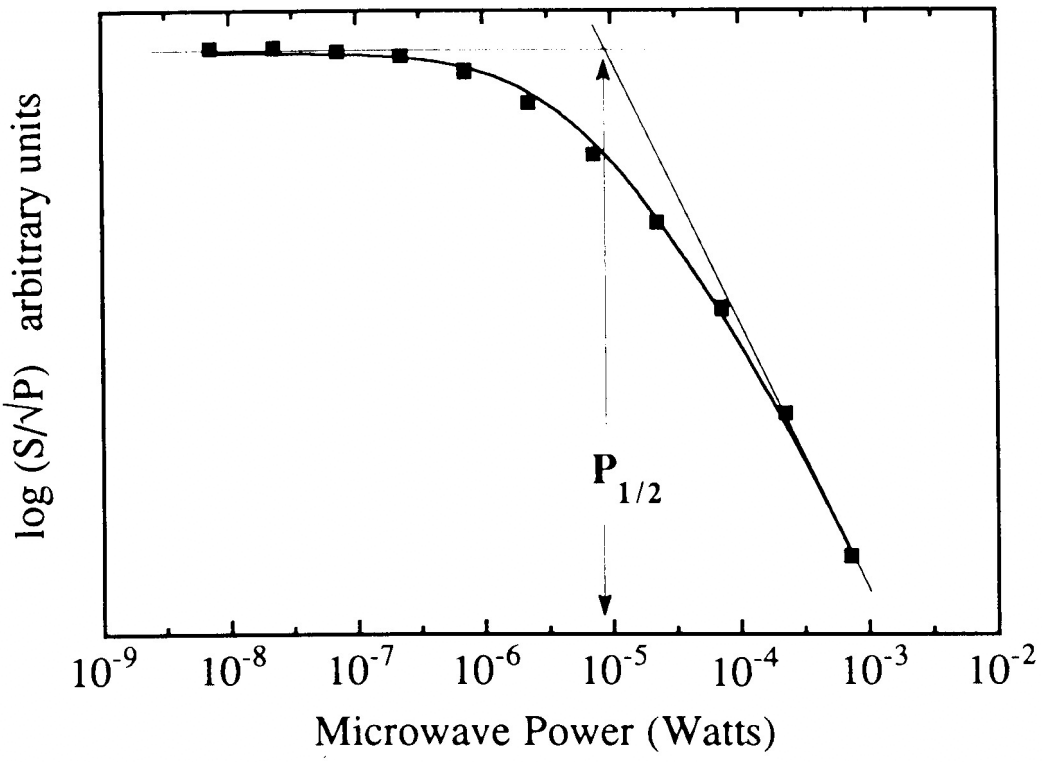
Experimental considerations

- EPR signal magnitude is proportional to population difference, which is dictated by a Boltzmann distribution
  - Low temperatures increase the population difference

k_BT at room temperature is 208 cm^{-1}, but EPR is usually done with 0.3 cm^{-1} radiation

- Population difference is depleted by microwave excitation and restored by intrinsic spin-lattice relaxation processes

  – Saturation can occur if the incident microwave power populates the excited state faster than it can be relaxed:



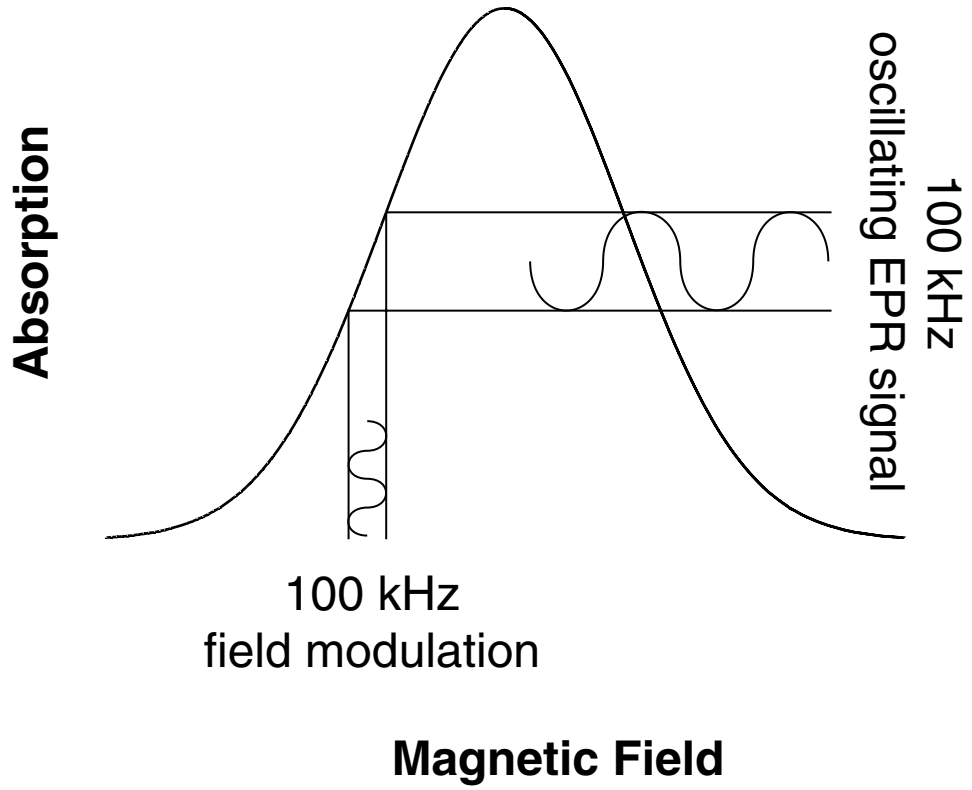
$I \propto \sqrt{S}$ under non-saturating conditions

Experimental considerations cont'd

- Room-temperature biological samples can be a problem, because water absorbs microwaves

  – Solution: freeze the sample or use a flat cell to place the water in the nodal plane of the *E*-field.

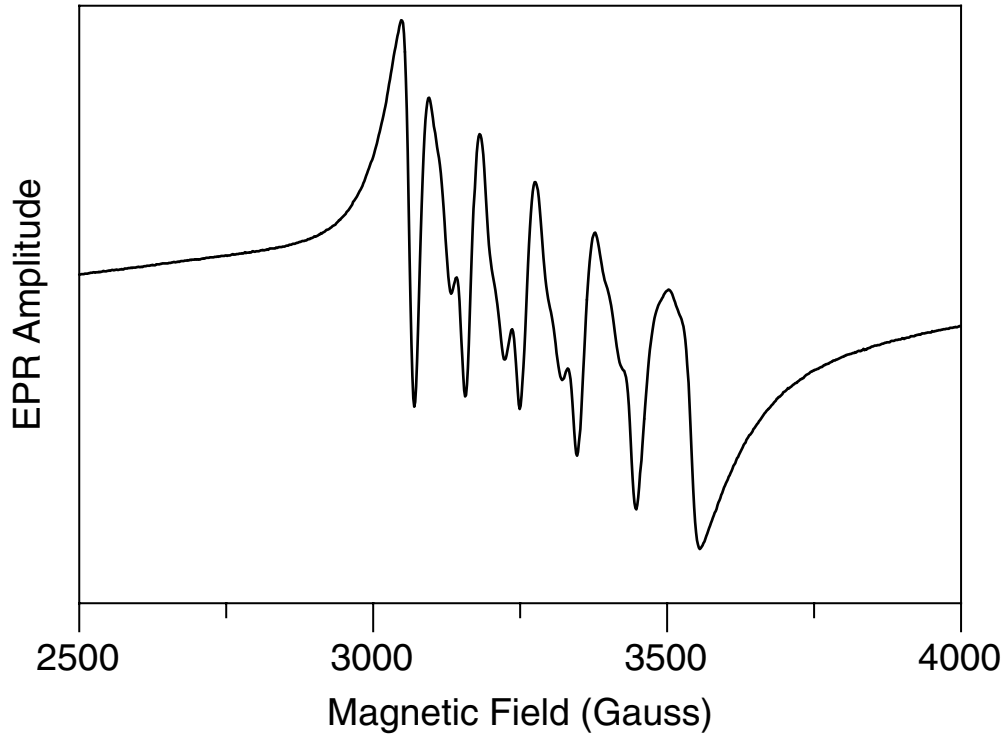
- Typical derivative presentation of EPR spectra is a consequence of the data acquisition method:



–lock-in detection greatly enhances signal-to-noise

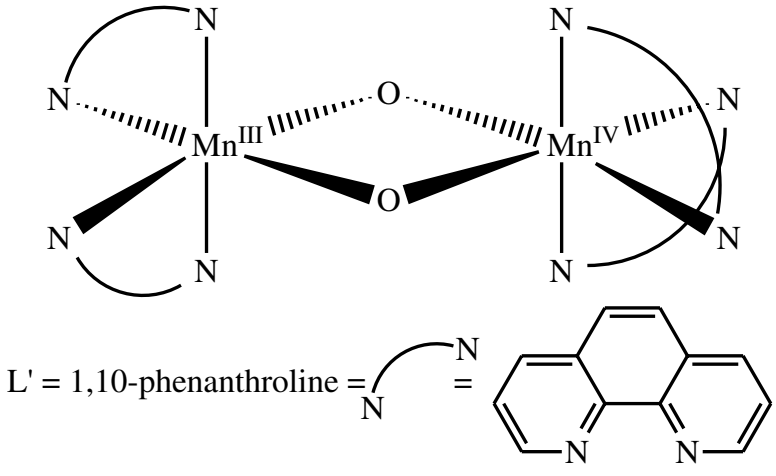
EPR spectra

$Mn^{2+}_{(aq)}$:



inclusion of the hyperfine term $\mathbf{A}\cdot\boldsymbol{I}\cdot\boldsymbol{S}$ for ^{55}Mn (I = 5/2) splits a single resonance into $2I+1$ lines

EPR spectrum of di-μ-oxo Mn(III/IV) phenanthroline (Cooper et al, JACS, 100, 7248-52):



- Because the two Mn ions are in different oxidation states, we expect that the hyperfine contributions to the spectrum will be different for each ion.

- Thus, this system is an example of hyperfine anisotropy in EPR

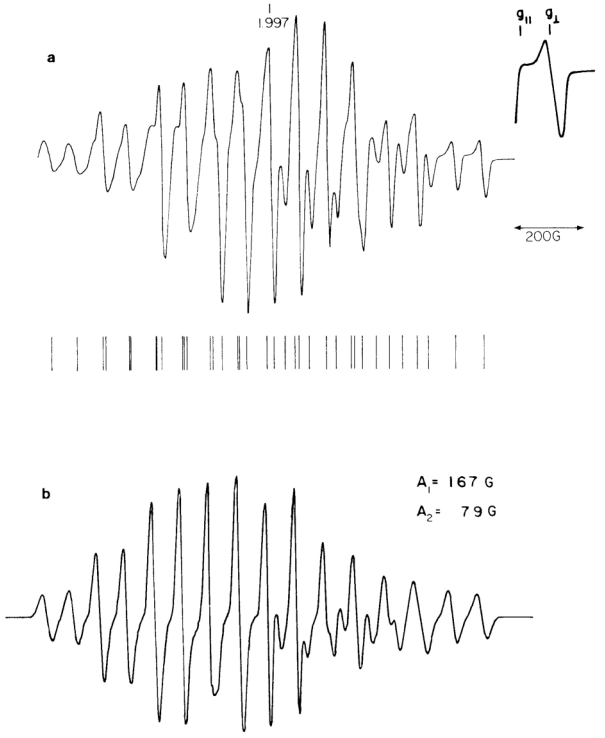
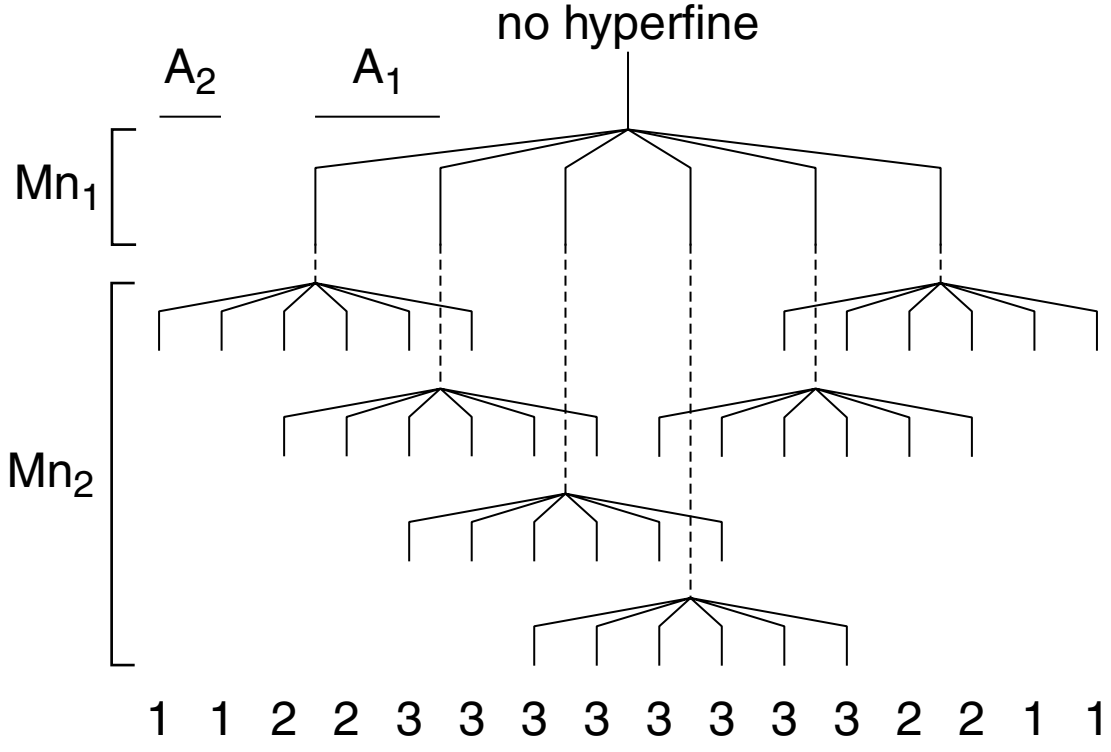
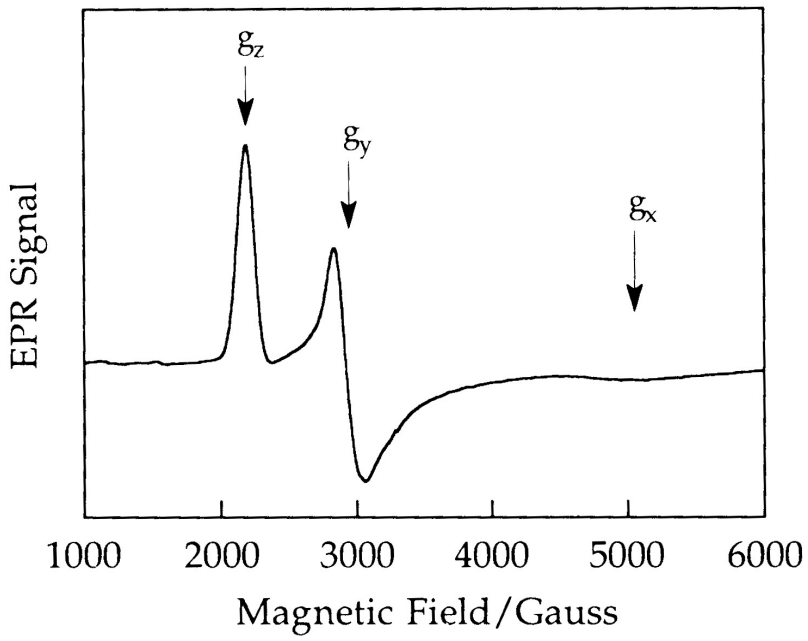


Figure 3. (a) EPR spectrum of phenanthroline(III,IV) dimer (10^{-3} M) in CH_3CN at 18 K. Microwave power 1.0 mW with 2 G modulation amplitude (100-kHz modulation frequency); microwave frequency 9.165 GHz. The inset shows an expanded region about the hyperfine peak at the high-field end of the spectrum. (b) Computer simulation of the (III,IV) EPR spectrum. The simulation was performed using a Gaussian line width which was a function of the nuclear quantum numbers m_1 and m_2: $\Delta = \Delta_0 + b_1 m_1 + b_2 m_2$, where $\Delta_0 = 5.5$ G, $b_1 = 2b_2 = 2.35$ G, and $2^{1/2}\Delta = \Delta H_{ms}$ = first derivative at maximum slope.

16-line spectrum can be largely explained if $A_1=2A_2$:



Another example: An Fe-containing heme protein
Fe^{3+}(l.s.) Cytochrome c



• This system displays *g* anisotropy and no hyperfine interactions

According to the Hamiltonian, *g* anisotropy is field-dependent, while hyperfine anisotropy is not.

This difference is exploited by performing EPR experiments at higher magnetic fields (and higher microwave energies).

Advantages:

• Restricts parameter space, because the same *g*, *A* parameters must fit the EPR spectra at all fields.

Other resonance techniques:

ENDOR (Electron-nuclear double resonance)

- excite nuclear transitions at the same time as exciting electron transitions, and look in the EPR spectrum for a change in absorption
  - **A** values can be obtained directly from the spectrum (in most cases), and are much more accurately determined than those from EPR experiments.

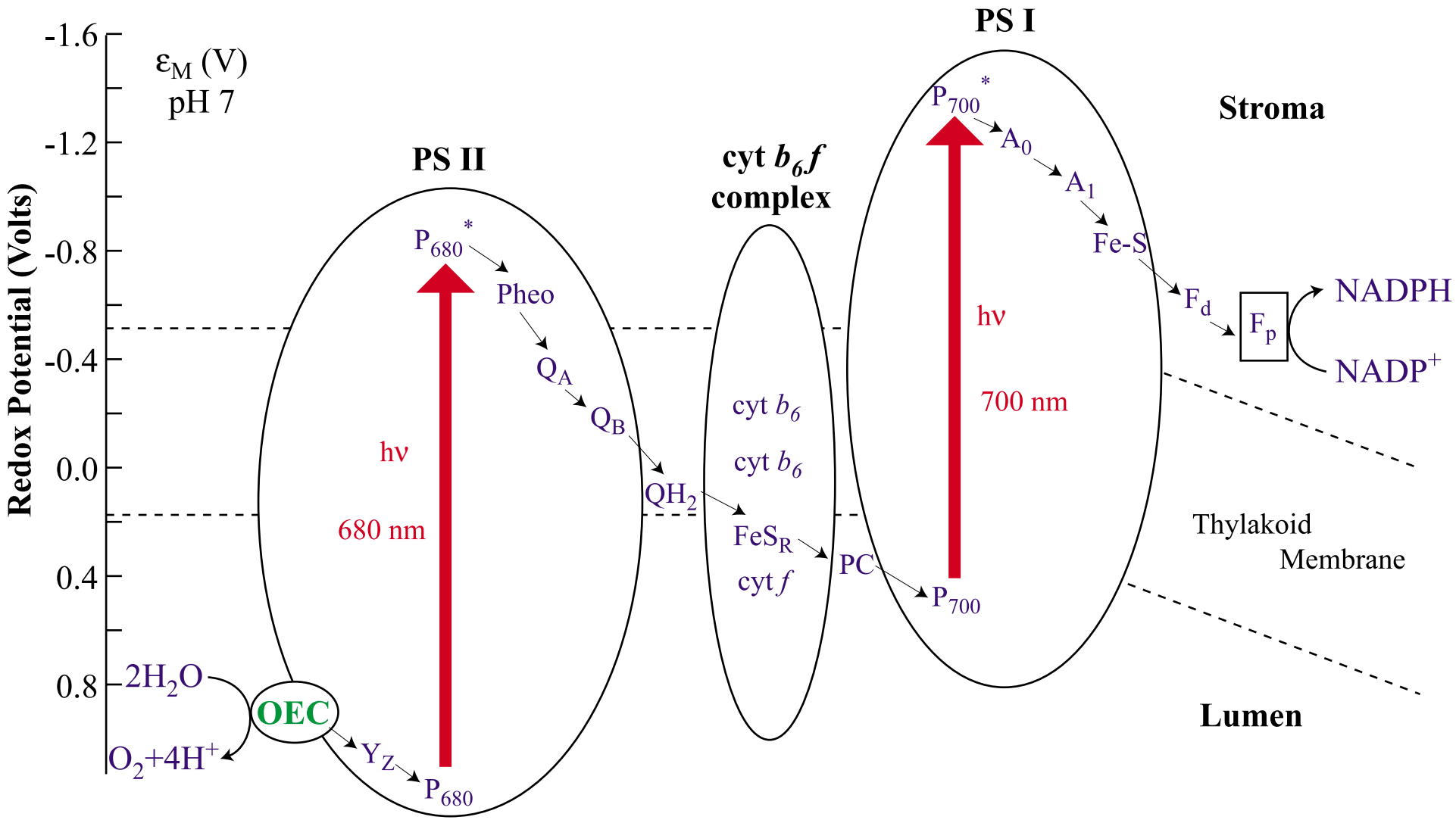
ESEEM (Electron spin echo envelope modulation)

- Excite a spin packet with a microwave pulse and watch its relaxation process using a Hahn spin echo experiment
  - A direct measurement of the spin-lattice relaxation time
  - Relaxation is modulated by other magnetic nuclei that are less than ~10 Å away

A wealth of information is available using EPR on paramagnetic systems

Z-scheme of photosynthetic electron flow

$$H_2O + CO_2 \rightarrow O_2 + (CHO)_n$$



Modified from: Miller, A.F., Brudvig, G. *Biochim. Biophys. Acta. 1056* (**1991**) 1.

Kok cycle of Photosystem II